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OBSERVATIONS AND MODELING OF NO_x IN AN URBAN AREA

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ABSTRACT

Data from the Regional Air Pollution Study are surveyed to delineate the experience with NO and NO_2 concentrations in St. Louis, a metropolitan area in the central United States. Two-year time series are produced for the daily maximum 1-h average in the monitoring network and the 24-h average of central urban sites. Various aspects of the data are displayed graphically including the time and location of the maximum, the distribution of concentration, and the relation of high concentrations to meteorological factors. A stagnation episode is examined in detail, and predictions of an air quality model are compared with measured levels of O_3, NO, NO_2, and CO.

INTRODUCTION

The Regional Air Pollution Study (RAPS), a major air quality assessment program of the U.S. Environmental Protection Agency (EPA), was conducted in St. Louis, Missouri, from late 1974 through early 1977 (refs. 1,2,3). St. Louis is a continental city of negligible topographic relief; about 2.3 million people reside in the metropolitan area. The principal objective of RAPS was to collect a comprehensive data base for use in evaluating air quality models designed to assess emissions-control strategies. Indeed, using RAPS data, extensive tests have been completed on models simulating the formation of photochemical O_3 (ref.4).

The central purpose of this paper is to characterize the measurements of NO and NO_2 taken over a two-year period during RAPS. This effort complements previous work conducted to characterize the O_3 record (ref.5), and results possibly can be extrapolated to many other U.S. cities with similar meteorological regimes, emissions composition, and lack of significant topographic features.

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*On assignment from the National Oceanic and Atmospheric Administration, U.S. Department of Commerce.

DATA BASE

Fig. 1 shows the St. Louis region with monitoring sites numbered 101-125. Each site had a tower of either 10 m or 30 m height, indicated by open or solid circles. Measurements included basic meteorological parameters as well as concentrations of pollutant gases, and data were recorded continuously as 1-min averages over the entire RAPS period. The 1-min data were later screened and used to form 1-h averages suitable for many research and modeling applications.

A chemiluminescent analyzer measured both NO and NO_x continuously with an intake manifold at about 4 m. The minimum detection limit was 5 ppb, and NO_2 was determined by differencing. Gas analyzers were automatically calibrated each day between the hours of 2000 and 2400 CST (local time).

The primary emphasis of this paper is on hourly NO and NO_2 concentrations recorded during all of 1975-1976. Notwithstanding the routine data screening done when the hourly archives were developed, there remained some obvious outliers. Computer scans of the data were used to print, for subsequent visual inspection, the highest and second-highest hourly concentrations recorded during each day. The second-highest was determined for a station

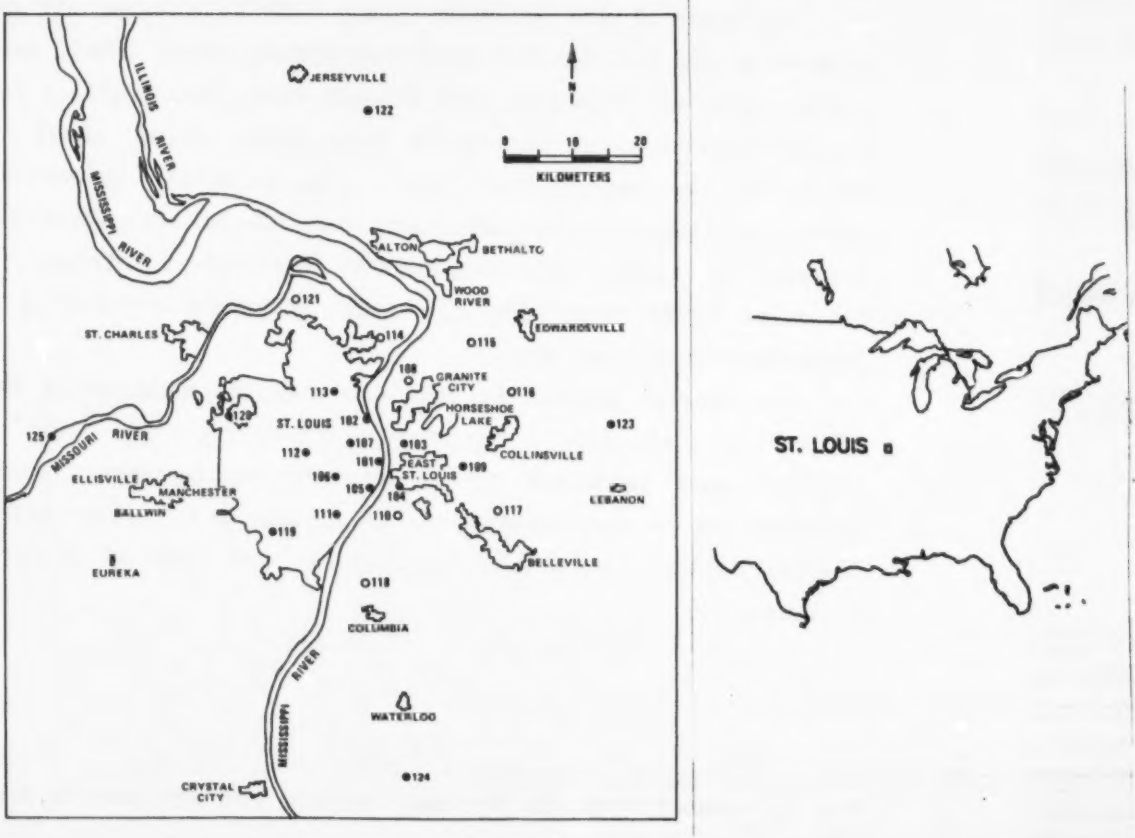

Fig. 1. The St. Louis region with locations of RAPS stations.

other than the station of the highest, since single stations tended to fail for several consecutive hours before being adjusted or removed. Experience with visual inspection led to maximum allowable differences between the highest and second-highest as a function of absolute concentration. For example, with NO_2 > 120 ppb it was unreasonable to allow the highest to be more than 50% larger than the second-highest, and, when this happened, the second-highest replaced the highest as the valid data point. Over the whole data base, valid daily maxima of NO and NO_2 were not found above 600 ppb and 300 ppb, respectively.

The locations of the RAPS stations were chosen to avoid the influence of local sources, and this was generally not a problem. However, site 102 showed substantial influence of a point source to the WNW, and maxima recorded with wind from that direction were discarded since they were not representative of areal averages.

Subject to the above editing, the hourly data base was scanned and basic information about the maxima of NO and NO_2 for each day was recorded on computer files for further analysis.

RESULTS FROM 1-HOUR AVERAGE DATA

Fig. 2 shows the distributions of daily maximum 1-h average concentrations of NO and NO_2 over the two-year period. As in all subsequent histograms and scatter plots, the number of data points (days) are printed in the upper right portion of the figure. While the peaks of both distributions are at less than 100 ppb, the distribution of NO has a substantial tail into higher concentrations. The difference likely reflects the role of NO as a primary emission which impinged directly on monitoring sites; NO_2, being secondary, was more diffuse.

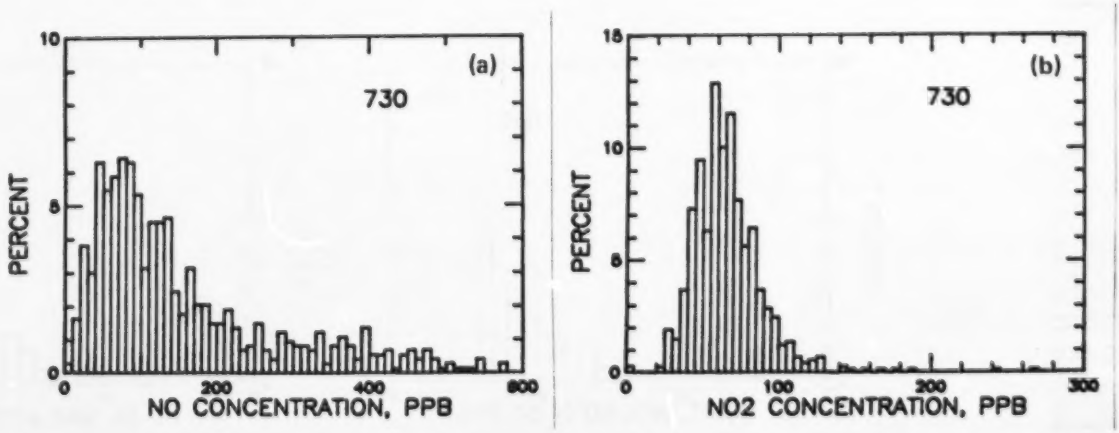

Fig. 2. Distribution of daily maximum 1-h concentrations from RAPS: (a) NO, (b) NO_2.

Fig. 3 shows the distributions of maxima by RAPS station (abbreviated 1-25). To emphasize the more significant values, only maxima above 60 ppb were used in forming this and subsequent figures. Generally the station distributions of NO and NO_2 are similar, probably reflecting the importance of automotive exhaust in the central city. The far-rural stations (122-125) almost always had values below the detection limit of the instruments. Site 101 was located near the center of the St. Louis business district. Notably, NO_2 maxima tended to occur more frequently than NO maxima at some outlying stations (e.g. 106, 112, 113, 114, and 121). This difference again was a consequence of the secondary nature of NO_2, and reflected transport away from the center of strongest NO emissions.

The distributions of the daily 1-h maxima with time of day indicate morning and evening peaks as seen in Fig. 4. Accumulation of NO during 0600-

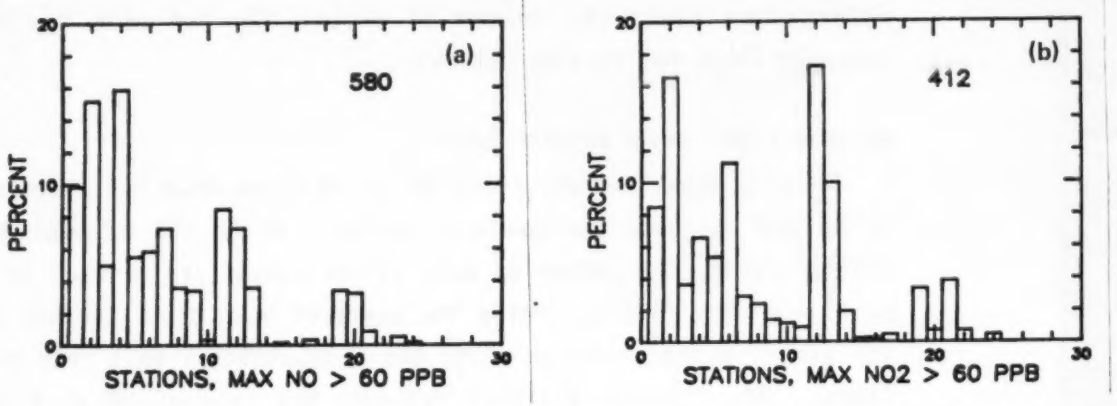

Fig. 3. Occurrence of daily maximum 1-h concentrations by RAPS station: (a) NO, (b) NO_2.

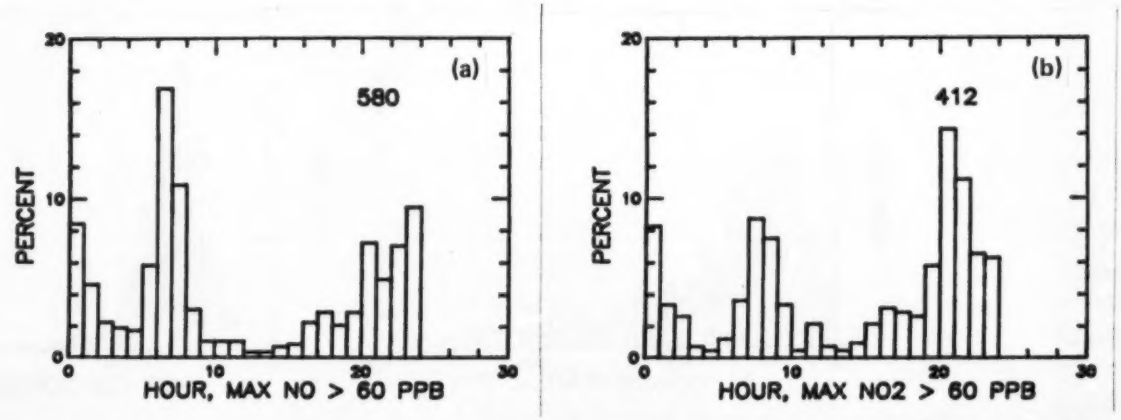

Fig. 4. Occurrence of daily maximum 1-h concentrations by hour of the day: (a) NO, (b) NO_2.

0700 CST resulted from rush-hour automotive exhaust trapped under a low morning mixing height. NO_2 reached a peak most frequently during the next hour as increasing solar radiation induced photochemical reactions, and, quite possibly, O_3 aloft was entrained by a rising mixing height. The decreasing mixing height in the evening again tended to trap pollutants near the surface. Ozone produced during the day rapidly oxidized NO emissions, with the net effect that NO_2 peaks were proportionately more frequent than NO peaks in the early evening. O_3 was depleted rapidly in the lower atmosphere as the evening progressed, and the frequency of NO_2 maxima decreased accordingly. Although these distributions represent the frequency of occurrences of the daily maxima, they can quite reasonably be thought of as displaying relative concentrations. That is, the more frequent occurrences of the daily maximum NO_2 during 2000-2100 CST would strongly suggest that concentrations tended to be higher, on the average, than for the morning peak. The well-defined diurnal cycles displayed in Fig. 4 (showing the behavior of NO and NO_2 concentrations relative to each other) are a consequence of both the length of the available record and the number of measurement stations in the network. For each day, the maximum was chosen from among all stations in the network, thus negating to some degree the confounding influence of advection. Even under the most extreme stagnations, it is difficult to identify the expected diurnal changes at a single site in such an unequivocal manner.

Fig. 5 shows the seasonal distributions of concentration maxima. As indicated on the figure, the lower limits for maxima entering the distributions were increased to emphasize high daily maxima. (Obviously, if all days were considered, the distributions would be uniform.) The seasonal changes in frequency of NO maxima can probably be explained by associated

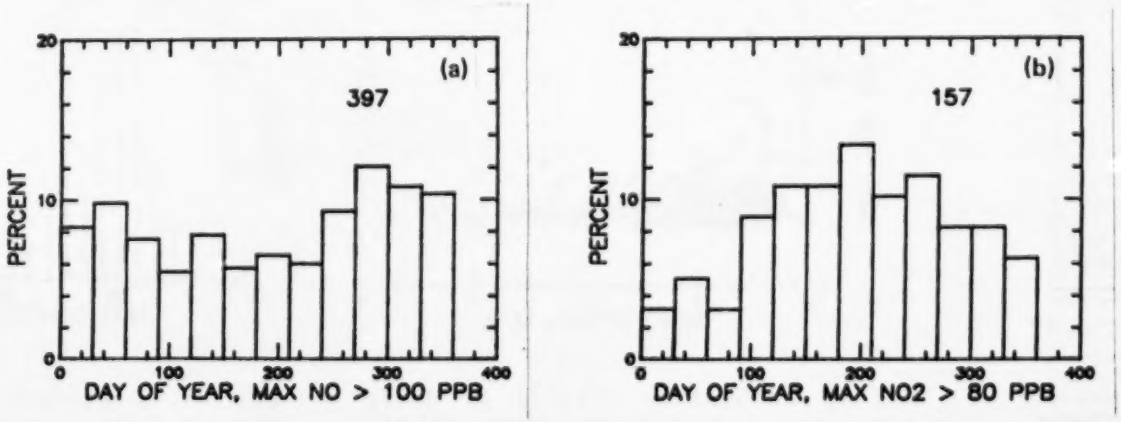

Fig. 5. Occurrence of daily maximum 1-h concentrations by 30-day segments of the year: (a) NO, (b) NO_2.

climatological conditions. The rise in frequency in the autumn was due to clear and dry conditions prevalent at that time. Those conditions are conducive to formation of strong nocturnal inversions that are very effective in trapping pollutants near the surface. Also, the shorter hours of daylight brought the stronger inversions closer to the rush-hour emissions peaks. The summer low resulted from greater atmospheric instability and the presence of higher O_3 levels, which diminished the possibility of strong NO maxima. On the other hand, the NO_2 distribution shows direct correlation of maxima with photochemistry active during the summer; the summertime enhancement of NO_2 maxima is complementary to the suppression of NO by O_3 oxidation.

Scatter diagrams were used to try to establish relationships between high concentrations of NO_2 and various meteorological parameters. Only wind speed seemed to have a clearly defined influence as seen in Fig. 6. Speed was defined from the network resultant over a 3-h period before the maximum. Only under very calm conditons were high NO_2 values recorded.

Finally, because of possible health effects, interest in NO_2 concentrations extends to averaging times beyond one hour. Therefore, 24-h average concentrations were computed, and a distribution is displayed in Fig. 7. The 24-h value was formed from all hourly data of stations 101, 102, 104, 105, 106, 112, and 113 (see Fig. 3b) and represents the spatial average of the central city over each day. The median concentration was about 25 ppb, and, given the shape of the distribution, the annual average would have a similar value.

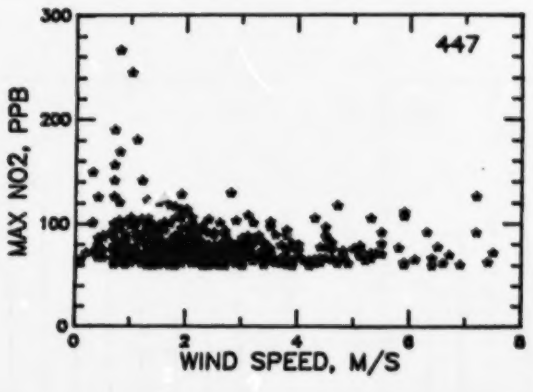

Fig. 6. Scatter diagram of daily maximum 1-h concentration of NO_2 versus network resultant wind.

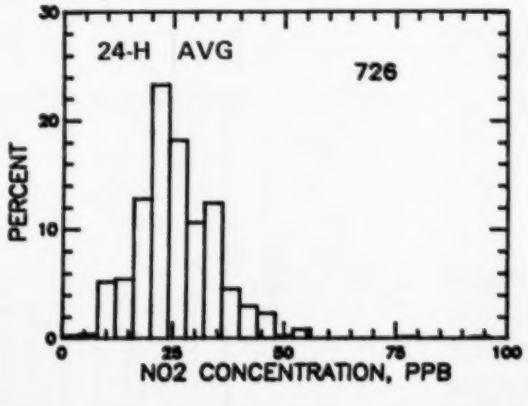

Fig. 7. Distribution of 24-h NO_2 concentrations averaged from hourly data of central stations (101, 102, 104, 105, 106, 112, and 113).

A STAGNATION EPISODE

The two highest hourly NO_2 values recorded during RAPS (see Fig. 6) occurred on 1 and 2 October 1976. In this section 1-min data are presented for the day of 1 October. Network winds remained at or below 1 m/s for the entire day, making this a unique stagnation during RAPS. Fig. 8 shows plots of 1-min average data from station 101 in the center of the city.

Solar radiation data indicate the day was very clear. The early morning surge in concentrations associated with automotive sources began about 0600 CST as seen from the NO and CO traces. The NO_2 build-up followed at about 0730 CST, and O_3 production was evident by 0900 CST. The disappearance of NO at 1130 CST coincided with a relative decrease in NO_2 and a rapid jump in O_3. With the approach of sunset and the set-up of the nocturnal inversion, NO_2 increased rapidly, presumably from oxidation of NO by residual O_3. NO levels rose only after depletion of O_3 by this reaction and surface deposition.

Routine instrument calibration resulted in some data gaps in the late evening. However, before midnight there was a sudden decrease in surface concentrations of NO and CO. This event was probably the result of transient vertical mixing, evident from an accompanying decrease in the stable vertical temperature gradient (not shown). Notably, NO_2 did not decrease at this time, indicating a more uniform vertical profile over the city. Evans has found (ref.6) that O_3 concentrations at a height of several hundred meters remain in the 60-100 ppb range during the night, while being negligible at the surface. Therefore, a large reservoir of O_3 is available to oxidize NO diffusing away from the surface and produce a deeper layer of NO_2.

PHOTOCHEMICAL MODELING OF 1 OCTOBER 1976

A series of tests on several photochemical models have been completed using 20 days of RAPS data (ref.4). Emphasis in those tests was on predicting the daily O_3 maximum, for which a 1-h National Ambient Air Quality Standard (NAAQS) of 120 ppb has been set (not to be exceeded more than once per year).

Results are presented here for a Lagrangian model (ref.7) which simulates a moving column of air having five vertical levels. The concentrations of pollutants are initialized in the column shortly after sunrise, and observed wind data are used to advect the column over emissions sources as the day progresses. Results are given only for 1 October 1976, the day for which the time series were presented in Fig. 8. Considering the calm conditions on that day, the meaning of a trajectory path is questionable, but basically the column meandered about within the city. The start position of the column was set so that it would reach station 102 at 1400 CST, the time and place of the observed O_3 maximum. The maximum observed NO_2 was at station 106 at 2200 CST, but the O_3 simulations were terminated before sunset.

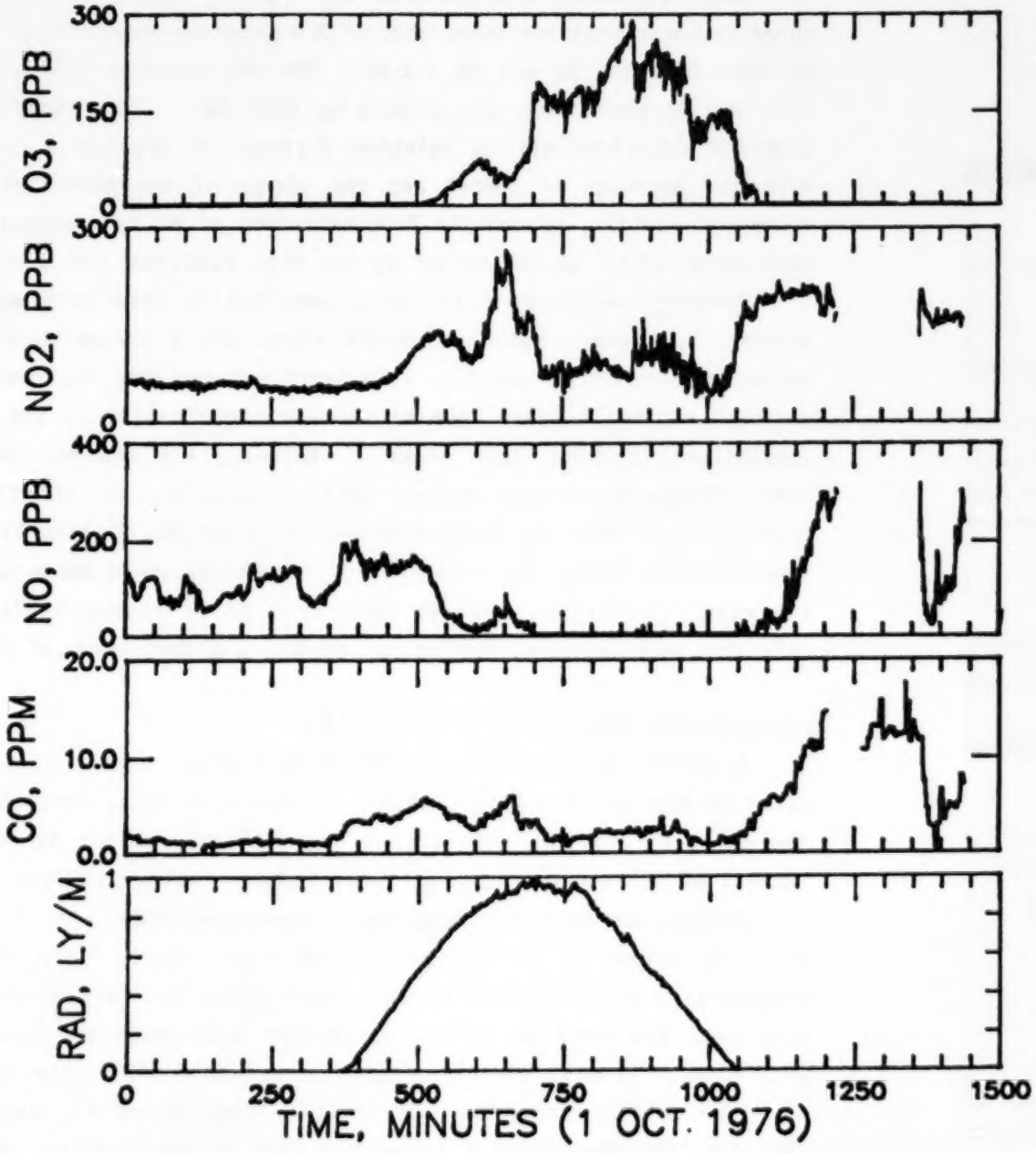

Fig. 8. Traces of 1-min data of 1 October 1976. Gas data are from station 101; solar radiation data are from stations 103 and 104. Time is measured in minutes from midnight.

Fig. 9 shows traces of observed and predicted O_3, NO, NO_2, and CO in the moving column. The observed values are based on data from the three stations closest to the column, and the predictions are for Level-1 (L-1, the surface) and Level-3 (L-3, about 200 m). For this model, L-1 has a tendency to rapidly accumulate surface emissions and give unrealistically high concentrations (e.g., NO). The errant L-1 predictions may serve as a reminder of the difficulties likely to be encountered when attempting complex modeling of urban photochemistry. Generally, L-3 concentrations are preferred since they are buffered from excursions caused by abrupt encounters with new surface sources. Using L-3 predictions, the ability of the Lagrangian model to simulate the photochemical system seems quite good considering the numerous approximations that are made. The L-3 NO_2 predictions track observations quite well in the 100-ppb range, and this result suggests that the model will be useful in air basins where such concentrations occur regularly. As presently constituted, the numerical scheme for solving chemical reaction equations is unable to handle the transition through sunset, and modeling of the evening NO_2 maximum is not possible.

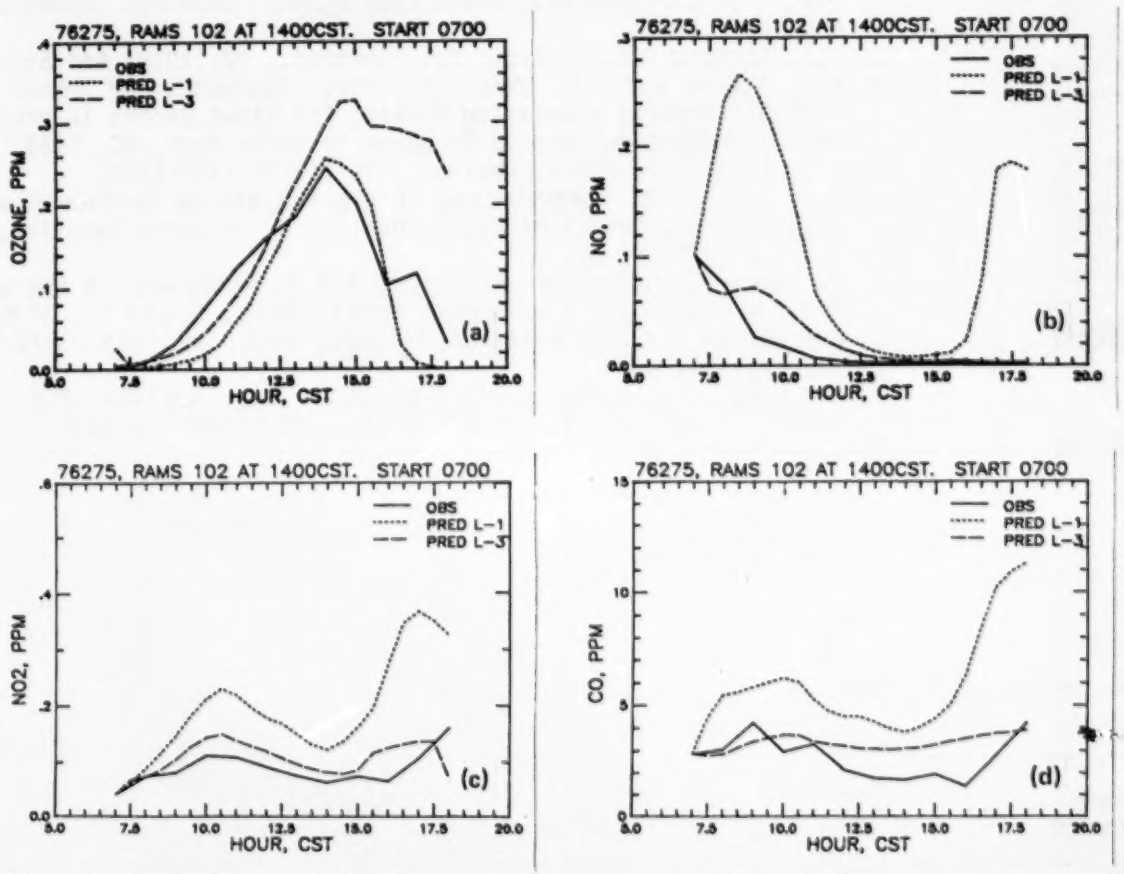

Fig. 9. Predicted and observed concentrations of O_3, NO, NO_2, and CO from a Lagrangian model simulation of 1 October 1976. Predicted concentrations are for the surface (L-1) and 200 m (L-3).

CONCLUDING REMARKS

The present NAAQS in the United States calls for limiting annual average NO_2 concentrations to 53 ppb. This standard was based largely on results of a study on lung performance of children exposed over long periods (ref.8). The RAPS data (see Fig. 7) indicate that no action would be necessary to meet the annual standard in St. Louis, and, by inference, other similar cities. Currently, there is some discussion on setting a standard for shorter averaging times, but firmer evidence of health risks associated with short-term exposure is needed. The State of California has set a 1-h standard for NO_2 of 250 ppb, and this level is exceeded regularly in the Los Angeles air basin (44 days in 1980). However, even the rather contained air basin around San Francisco showed only one violation of the standard in 1980, a rate that might be projected for St. Louis based on the RAPS data.

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